

and a ring as they exhibit only end absorption curves for ultraviolet spectra and are readily hydrogenated catalytically to hexahydro derivatives as shown by mass spectrometry. Compound C is concluded to be **4** as it is dextrorotatory and has an identical gas chromatographic retention time⁸ and proton nmr spectrum. The proton nmr spectrum of compound A, $[\alpha]^{23.5D} +28^\circ$ (CCl_4 , c 0.0036), clearly shows the presence of an ethyl group connected to an olefinic methine (triplet at δ 0.96 and a quintet at δ 2.05, $J = 7.5$ Hz) and a vinyl group (doublet of multiplets at δ 4.89, $J = 10$ Hz for *cis* coupling, and a doublet of multiplets at δ 4.93, $J = 17$ Hz for *trans* coupling; J_{gem} estimated to be 2.5 Hz). The proton nmr spectrum of compound B, $[\alpha]^{23.5D} +105^\circ$ (CCl_4 , c 0.002), however, shows instead a methyl group connected to an olefinic methine (doublet at δ 1.63, apparent $J = 5$ Hz) in addition to a vinyl group (doublet of multiplets at δ 4.87, $J_{\text{cis}} = 10$ Hz, and a doublet of multiplets at δ 4.91, $J_{\text{trans}} = 17$ Hz, J_{gem} again estimated to be 2.5 Hz). These findings, coupled with biogenetic arguments (see below), suggested that compound A is a 4-vinyl-5-(1'-butenyl)cyclopentene and that compound B is a 4-vinyl-5-propenylcyclohexene. Detailed analysis of the proton nmr spectra¹⁰ verified these conclusions and in addition established the stereochemistry of both compounds.

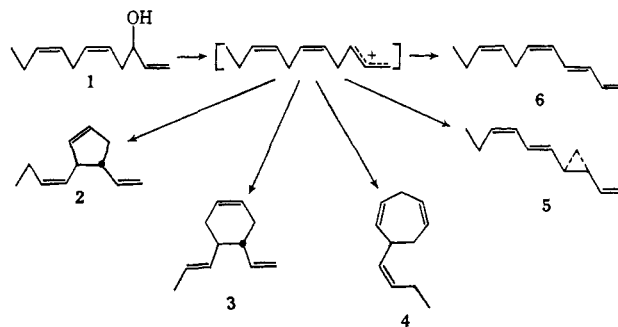
The most salient features of the nmr spectrum of compound A are the following. (1) Long range coupling ($J = 1$ Hz) in the quintet at δ 2.92 for the C-4 proton and the doublet of multiplets at δ 4.89 and 4.93 for the terminal methylene protons shows that the vinyl group is attached to C-4. (2) The triplet of multiplets at δ 3.56 is assigned to the C-5 methine proton and reflects large vicinal coupling ($J = 8.5$ Hz) to the C-4 ring protons and the C-1 olefinic proton in the butenyl side chain, a small vicinal coupling ($J \approx 2$ Hz) to the C-1 ring proton, and long range coupling to several protons. (3) The geometry of the double bond in the butenyl side chain is *cis* as the C-2' proton which resonates as a doublet of triplets at δ 5.33 interacts with the C-1' proton, which appears as a doublet of doublets at δ 5.06, by 11 Hz. Finally, the vinyl and butenyl substituents are tentatively assigned to have a *trans* relationship.

The nmr spectrum of B, on the other hand, has the following important characteristics. (1) Six protons absorb in a broad multiplet at δ 1.99 and this signal is attributed to the C-3 and C-6 methylene protons and the axially disposed (therefore *trans* to each other) C-4 and C-5 methine protons. (2) The geometry of the propenyl side chain is *trans*, since the C-1' and C-2' proton interaction is 17 Hz as shown from the doublet of quartets for the C-2' proton at δ 5.32. (3) The chemical shifts of most of the ring protons and vinyl protons are comparable with those of vinyl cyclohexene.¹¹

From these data it is clear that compound A is *trans*-4-vinyl-5-(*cis*-1'-butenyl)cyclopentene (**2**) and that compound B is *trans*-4-vinyl-5-(*trans*-1'-propenyl)cyclohexene (**3**). We propose the names multifidene for the

biologically active **2** and aucantene (Latin for "Vogel-sang" where the compounds were isolated first) for the biologically inactive **3**.

The two new hydrocarbons from *Cutleria* are obviously biogenetically related to the C_{11} hydrocarbons,¹² C_{11} ketones,¹³ and sulfur compounds¹⁴ from Hawaiian *Dictyopteris*. *cis,cis*-Undeca-1,5,8-trien-3-ol (**1**) may



serve as a common intermediate¹⁵ since it satisfactorily explains the formation of all the algal $\text{C}_{11}\text{H}_{16}$ hydrocarbons (**2**, **3**, **4**, **5**,^{12b} **6**^{12b}) isolated to date, including the C_8 hydrocarbon fucoserratene.¹⁶

Acknowledgment. We thank Miss E. Fölster for skilled technical assistance and the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support.

(12) (a) R. E. Moore, J. A. Pettus, Jr., and M. S. Doty, *Tetrahedron Lett.*, 4787 (1968); (b) J. A. Pettus, Jr., and R. E. Moore, *Chem. Commun.*, 1093 (1970).

(13) R. E. Moore and G. Yost, *J. Chem. Soc., Chem. Commun.*, 937 (1973).

(14) (a) P. Roller, K. Au, and R. E. Moore, *Chem. Commun.*, 503 (1971); (b) R. E. Moore, *ibid.*, 1168 (1971); (c) R. E. Moore, J. Mistysyn, and J. A. Pettus, Jr., *ibid.*, 326 (1972).

(15) Discussed by R. E. Moore at the Symposium on the Chemistry of Essential Oils, 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973. See Abstract No. AGFD 056 for a scheme outlining the biogenesis of the $\text{C}_{11}\text{H}_{18}$ hydrocarbons and certain ketones and sulfur compounds in Hawaiian *Dictyopteris* from *cis*-undeca-1,5-dien-3-ol.

(16) The biogenesis of fucoserratene, a 1,3,5-octatriene,⁵ can also be rationalized from **1** if the latter is first oxidized at C-7 to *cis,cis*-undeca-1,5,8-triene-3,7-diol. Subsequent heterolytic fragmentation [C. A. Grob and P. W. Schiess, *Angew. Chem.*, **79**, 1 (1967); *Angew. Chem. Int. Ed.*, **6**, 1 (1967)] then results in acrolein and *trans,cis*- or *cis,cis*-1,3,5-octatriene. Synthetic work [L. Jaenicke and K. Seferiadis, unpublished results] establishes that fucoserratene is *trans,cis*-1,3,5-octatriene.

(17) Work done while on sabbatical leave at the Institut für Biochemie der Universität zu Köln, Germany. Financial assistance from the National Science Foundation (GP 29412) and the donors of the Petroleum Research Fund (5514-AC1), administered by the American Chemical Society, is gratefully acknowledged.

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Reactive Transition Metal Dinitrosyl Complexes. Synthetic Uses and Catalytic Properties

Sir:

For a variety of reasons, not the least of which are environmental, there is obvious interest in reactions

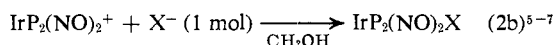
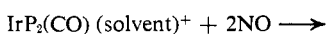
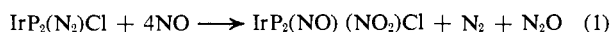
(10) Proton assignments were confirmed by appropriate spin-spin-decoupling experiments.

(11) The nmr spectra of compound B and 4-vinylcyclohexene were compared directly. We found that chemical shifts for 4-vinylcyclohexene differed slightly with those reported in the Varian High Resolution NMR Spectra Catalog, Vol. I, 1962.

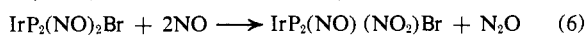
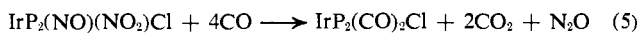
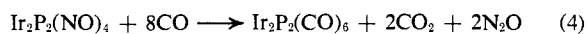
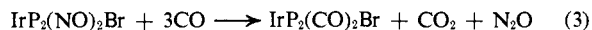
which convert NO and CO into less noxious products. Prompted by recent results of other workers, we wish to report a series of reactions and experiments which suggest that certain dinitrosyl complexes are unexpectedly reactive and that the conversion of NO and CO into N₂O and CO₂ in their presence is catalytic and general in scope. We also describe the ready syntheses of some related compounds which were previously more difficult to synthesize.

Johnson and Bhaduri¹ have reported the production of CO₂ and N₂O from the reaction of CO with [IrP₂(NO)₂][PF₆]₂,² forming [IrP₂(CO)₂][PF₆]₂ which in turn reacts with NO to regenerate the dinitrosyl "thereby allowing a continuous oxidation-reduction process to take place"; these authors postulate a nitrene complex as a possible intermediate in these reactions. Reed and Eisenberg³ have also noted that NO and CO passed through solutions of some Rh(III) compounds yield N₂O and CO₂ in a catalytic cycle.

In an earlier effort to develop simplified syntheses for IrP₂(NO)₂X (X = Br, I, NCO, and N₃) the following reactions were carried out⁴



The surprising production of N₂O in (1) also occurs using IrP₂(CO)Cl and IrP₂(CO)₂Cl; similar reactions involving IrP₃Cl,⁸ RhP₃Cl,^{9,10} and RhP₂(CO)Cl⁹ also take place. Reaction 2a also proceeds with RhP₂(CO)(acetone)⁺, as well as with IrP₂(CO)₃⁺.¹ In order to elucidate reaction 1 we carried out the following reactions



(1) B. F. G. Johnson and S. Bhaduri, *J. Chem. Soc., Chem. Commun.*, 650 (1973).

(2) Abbreviations used are: P = triphenylphosphine, en = ethylenediamine.

(3) J. Reed, Jr., and R. Eisenberg, *Science*, in press.

(4) Reactions described here were carried out at room temperature in benzene, acetone, or chloroform under 1 atm of NO or 1–3 atm of CO in a closed reaction vessel, with PF₆⁻ or BF₄⁻ as anions, if appropriate. Gaseous products were identified by their gas-phase infrared spectra and chromatographic retention times. The complexes were unequivocally identified by comparing them with identical complexes prepared by other means. In reactions 3 and 5 another unidentified Ir–CO complex also forms to the extent of about 10%. Other reactions, except (11) which is catalytic, were stoichiometric. Quantities of gaseous products, but not reactants, were determined chromatographically. Elemental analyses were satisfactory. Magnetic measurements were performed using a Faraday balance.

(5) M. Angoletta and G. Caglio, *Gazz. Chim. Ital.*, **93**, 1584 (1963).

(6) W. Beck and K. v. Werner, *Chem. Ber.*, **106**, 868 (1973).

(7) Even when reaction 2b is carefully carried out, the product contains 5–20% of IrP₂(NO)X₂. IrP₂(NO)₂Br (ν(NO) = 1540 and 1500 cm⁻¹) is diamagnetic; owing to decomposition in solution, accurate molecular weights could not be obtained nor could crystals sufficiently large for diffraction work be grown. The values of ν(NO) preclude the formulation of this compound as a hyponitrite complex. See S. Cenini, R. Ugo, G. LaMonica, and S. D. Robinson, *Inorg. Chim. Acta*, **6**, 182 (1972), and references therein.

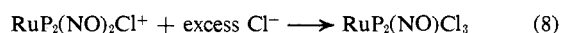
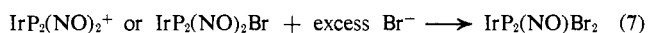
(8) M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, **91**, 6983 (1969).

(9) W. B. Hughes, *Chem. Commun.*, 1126 (1969).

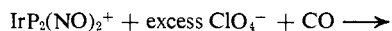
(10) K. Jitsuo, S. Yoshikawa, and J. Furukawa, *Bull. Chem. Soc. Jap.*, **43**, 3614 (1970). Results here and in ref 9 and 10 are in direct contrast to Y. N. Kukushin and M. M. Singh, *Zh. Neorg. Khim.*, **14**, 3167 (1969); **15**, 2741 (1970).

In contrast to the Ir and Rh complexes, MP₂(NO)₂ (M = Ru and Os) is found to react only very slowly with CO at room temperature. The synthetic utility of these reactions is illustrated by (4), which affords essentially a quantitative preparation of Ir₂P₂(CO)₆, starting with Ir₂P₂(NO)₄,^{11,12} which in turn is prepared conveniently in good yield from IrP₂H₃.¹³ Previously, preparations of Ir₂P₂(CO)₆ were carried out under high pressure (≈ 100 atm) or yielded mixed products.¹⁴

Reactions 3 and 6 show that both CO and NO can act as reducing agents. Furthermore, reaction 6, which also proceeds with the Rh analog,¹⁰ suggests that cis-nitro nitrosyl complexes behave in much the same manner as dinitrosyl complexes. Reduction of nitro complexes by CO or phosphines to form nitrosyl complexes is well known.¹⁵ In substitution reactions, CO is not generally known to displace NO, and the apparently anomalous behavior observed above is also observed in reactions 7 and 8 where a halide anion displaces NO.

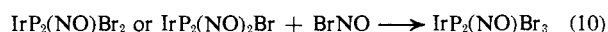


Although IrP₂(NO)₂(CO)⁺ could not be isolated, this or a similar intermediate is inferred from reaction 9, which



does not take place in the presence of other nonoxidizing, noncoordinating anions, such as PF₆⁻ or BF₄⁻. Under such reaction conditions ClO₄⁻ reacts neither with CO nor with IrP₂(NO)₂⁺ alone.

In the presence of certain oxidizing agents, IrP₂(NO)₂X (X = Cl and Br) is quantitatively converted into the 19-electron paramagnetic (1.3 BM) species IrP₂(NO)X₃ (reaction 10), which is a monomeric non-



conductor in solution, ν(NO) = 1732 cm⁻¹ (X = Cl). IrP₂(NO)Cl₃ appears to be isostructural (I2/a, Z = 4) with OsP₂(NO)Cl₃¹⁶ (ν(NO) = 1850 cm⁻¹) and with IrP₂(NO)Cl₂ (ν(NO) = 1560 cm⁻¹) and probably differs only in that the NO is "half bent," rather than being linear or fully bent. Similar reactions may also be carried out in excellent yield with IrP₃(NO), IrP₂(NO)₂⁺, IrP₂(NO)Cl⁺, IrP₂(N₂)Cl, and IrP₃Cl. In certain cases ClNO or Br₂ may be used in place of BrNO.⁵ When used in excess, Cl₂ readily carries the oxidation further to the paramagnetic complex IrP₂Cl₄.¹⁷

The above reactions implicate transition metal dinitrosyls as the important species in the reduction of NO by CO. To test the generality of this reaction (11), it was

(11) M. Angoletta, *Gazz. Chim. Ital.*, **93**, 1591 (1963).

(12) M. Angoletta, G. Ciani, M. Manassero, and M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 789 (1973).

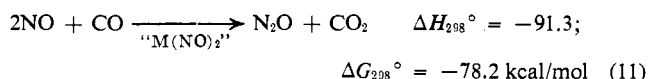
(13) A convenient high yield synthesis of IrP₂H₃ (ν(Ir–H) = 2144 and 1951 cm⁻¹) from IrP₂(N₂)Cl and BH₄⁻ will be published elsewhere. For Ir₂P₂(NO)₄, ν(NO) = 1674 and 1642 cm⁻¹; for Ir₂P₂(CO)₆, ν(CO) = 2021, 1979, 1951, and 1933 cm⁻¹.

(14) R. Whyman, *J. Organometal. Chem.*, **24**, C35 (1970); L. Malatesta, M. Angoletta, and F. Conti, *ibid.*, **33**, C43 (1971).

(15) R. D. Feltham, *Inorg. Chem.*, **3**, 116 (1964); K. R. Grundy K., R. Laing, and W. R. Roper, *Chem. Commun.* 1500 (1970); G. Booth and J. Chatt, *J. Chem. Soc.*, 2099 (1962).

(16) The structure of the Ru analog, RuP₂(NO)Cl₃ (ν(NO) = 1880 cm⁻¹) shows a completely linear NO: B. L. Haymore and J. A. Ibers, unpublished results. IrP₂(NO)Cl₃⁺ (ν(NO) = 1945 cm⁻¹) is known, but not IrP₂(NO)Cl₃⁻.

(17) C. A. Reed and W. R. Roper, *J. Chem. Soc. A*, 3054 (1970).



carried out in the presence of $\text{IrP}_2(\text{NO})_2\text{Br}$, $[\text{IrP}_2(\text{NO})_2]\text{PF}_6$, $\text{IrP}_2(\text{CO})(\text{solvent})^+$, and their Rh analogs. The reactions proceed catalytically, albeit slowly, at 20° . For example, with $[\text{RhP}_2(\text{NO})_2][\text{PF}_6]$ after 170 hr there is a 62% conversion of reactants to products with 126 mol of N_2O produced per mole of Rh.¹⁸ $\text{IrP}_2(\text{NO})\text{Br}_2$, $\text{CoP}_2(\text{NO})_2\text{Br}$, and $[\text{CoP}_2(\text{NO})_2][\text{PF}_6]$ were found to be inactive.

The anomalous reactivity and catalytic properties of certain four- and five-coordinate dinitrosyl complexes suggest to us that many of the "20-electron" dinitrosyls, at least while intermediates in these reactions, may be better formulated as 18-electron, N,N-bonded, cis-dinitrogen dioxide (not hyponitrite) complexes in which there is a significant N-N interaction; thus, for example, $\text{IrP}_2(\text{NO})_2\text{Br}$ would become $\text{IrP}_2(\text{N}_2\text{O}_2)\text{Br}$. This alternate suggestion differs from the nitrene postulate¹ in that the N-N interaction is formed before rather than after oxygen abstraction. Dinitrogen dioxide intermediates, such as $\text{Ni}(\text{CO})_2(\text{N}_2\text{O}_2)$ and $\text{Co}(\text{en})_2(\text{N}_2\text{O}_2)^{2+}$, may also be involved in the conversion of $\text{Ni}(\text{CO})_4$ to $\text{Ni}(\text{NO})(\text{NO}_2)$ and *trans*- $\text{Co}(\text{en})_2(\text{NO})\text{Cl}^+$ to *cis*- $\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}^+$ by NO .¹⁹ Efforts to confirm such a scheme by isolating possible intermediates and by studying reaction 11 under varying conditions are continuing.

Acknowledgments. We are indebted to Mr. J. Reed, Professor R. Eisenberg, and Professor R. L. Burwell, Jr., for helpful discussions and to Matthey Bishop, Inc., for the generous loan of precious metals used in this study. This research was supported by the Advanced Research Projects Agency and the National Science Foundation through the Northwestern University Materials Research Center.

(18) Reaction conditions: Initial absolute pressure was 2.99 atm (corrected for the vapor pressure of solvent, 2-butanone); temperature was 20° ; mole ratio of CO to NO was 1.1:2.0; 90 mg of Rh complex was used; $P_{\text{N}_2\text{O}} = P_{\text{CO}_2}$, within experimental error (3%); reactions were carried out in a closed stainless steel-glass reaction vessel. There was no reaction under identical conditions in the absence of the Rh complex.

(19) D. Gwost and K. G. Caulton, Abstract, 166th ACS Meeting, Chicago, Ill., Aug 1973, No. INOR-102; R. D. Feltham, *Inorg. Chem.*, **3**, 121 (1964).

Barry L. Haymore, James A. Ibers*

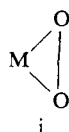
Department of Chemistry and The Materials Research Center
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Received December 31, 1973

SCF-X α Scattered Wave Calculation of the Electronic Structure of $\text{Pt}(\text{PH}_3)_2(\text{O}_2)$

Sir:

The metal-dioxygen bond in transition metal complexes containing chelated molecular oxygen (i) is



usually described qualitatively¹ as a combination of "forward donation" from filled O_2 $1\pi_u$ orbitals to

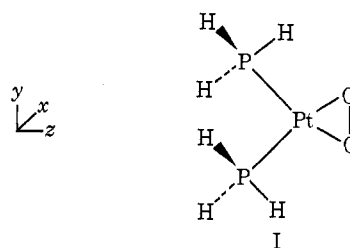
(1) F. R. Hartley, *Angew. Chem., Int. Ed. Engl.*, **11**, 596 (1972).

empty orbitals on the metal and "back-donation" from filled metal d orbitals to the half-filled O_2 $1\pi_g$ antibonding levels. Mason² notes that the resulting electronic configuration for O_2 approximates the first excited state of the free molecule, about one electron having been removed from the $1\pi_u$ orbitals (by forward donation) and added to the $1\pi_g$ orbitals (by back-donation). The O-O bond lengthening invariably observed upon chelation of dioxygen to a transition metal³ is explained as due to this replacement of bonding by antibonding electron density.

Dioxygen seems particularly suited among diatomic molecules to accept electrons from metals by π back-donation, since the half-filled character of its $1\pi_g$ orbitals brings them into the same energy range as filled metal d π orbitals, and d π - π_g overlap might therefore be efficient. This contrasts with such ligands as CO and ethylene, where the antibonding ligand π orbitals are empty. No quantitative calculations are available for metal-dioxygen complexes to aid in assessing the importance of back-donation therein. I report here such a study for dioxygenbis(phosphine)platinum, $\text{Pt}(\text{PH}_3)_2(\text{O}_2)$, an approximate model for the known compound $\text{Pt}(\text{PPh}_3)_2(\text{O}_2)$,⁴ which is a simple, stable dioxygen complex whose X-ray structure is established.⁵ The formally zerovalent platinum atom and relatively long O-O bond (1.51 Å; cf. 1.21 Å in free O_2) suggest that, if π back-donation is important in any dioxygen complex, it should be here.

The X α scattered-wave (X α SW) method, which has been thoroughly reviewed,⁶ was employed for this calculation. Briefly, it is a *first principles* self-consistent-field method which yields one-electron eigenvalues in excellent agreement with experiment, being equal or superior in this respect to the best *ab initio* calculations, but which requires only a small fraction of the computer time of even approximate Hartree-Fock treatments. The main applications of the X α SW method will probably be with large molecules, for which complete, accurate, and nonempirical calculations have previously been prohibitively expensive.

$\text{Pt}(\text{PH}_3)_2(\text{O}_2)$ was calculated in conformation I,



corresponding to the highest possible symmetry, C_{2v} . Dimensions were taken from the known structures of $\text{Pt}(\text{PPh}_3)_2(\text{O}_2)$ ⁵ and PH_3 .⁷ All valence and core levels

(2) R. Mason, *Nature (London)*, **217**, 543 (1968).

(3) (a) J. S. Valentine, *Chem. Rev.*, **73**, 235 (1973); (b) V. J. Choy and C. J. O'Connor, *Coord. Chem. Rev.*, **9**, 145 (1972).

(4) C. D. Cook and G. S. Jauhal, *J. Amer. Chem. Soc.*, **90**, 1464 (1968).

(5) P. T. Cheng, C. D. Cook, S. C. Nyburg, and K. Y. Wan, *Can. J. Chem.*, **49**, 3772 (1971).

(6) (a) K. H. Johnson, *Advan. Quantum Chem.*, **7**, 143 (1973); (b) K. H. Johnson, J. G. Norman, Jr., and J. W. D. Connolly in "Computational Methods for Large Molecules and Localized States in Solids," F. Herman, A. D. McLean, and R. K. Nesbet, Ed., Plenum Press, New York, N. Y., 1972, pp 161-201; (c) J. C. Slater and K. H. Johnson, *Phys. Rev. B*, **5**, 844 (1972).

(7) (a) K. Kuchitser, *J. Mol. Spectrosc.*, **7**, 399 (1961); (b) M. H. Sivertz and R. E. Weston, Jr., *J. Chem. Phys.*, **21**, 898 (1953).